UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
CENTER FOR ENVIRONMENTAL MEASUREMENT AND MODELING
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OFFICE OF
RESEARCH AND DEVELOPMENT

April 23, 2020

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Subject: NJ DEP Report #6: Targeted Analysis of PFCA in Vegetation Samples

Dear Mr. Kloo:

I am pleased to provide you with this laboratory report of targeted analysis results for perfluorinated carboxylic acid (PFCA) concentrations in vegetation. This is the 6th in a series of reports prepared as a part of EPA Office of Research and Development's (ORD) collaboration with the New Jersey Department of Environmental Protection (NJ DEP) and EPA Region 2 on the study, "Detection, Evaluation, and Assignment of Multiple Poly- and Perfluoroalkyl Substances (PFAS) in Environmental Media from an Industrialized Area of New Jersey." This report includes concentration results for PFCAs in 24 vegetation samples based on analysis with known standards.

It is our understanding that this information was requested by NJ DEP to help in their ongoing investigation into the presence of PFAS in the environment near manufacturing facilities of interest. This request relates to our research capabilities and interests applying targeted and non-targeted analysis methods for discovery of the nature and extent of PFAS environmental occurrence that may be potentially associated with industrial releases. EPA continues to develop analytical methods for many PFAS compounds in various media including some of those included in this report. We are providing the results of our analysis as they become available.

In this report, we do not interpret exposure or risk from the values presented in this report. EPA does not currently have health-based standards, toxicity factors, or associated risk levels for PFAS, other than perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorobutanesulfonic acid (PFBS). While the data provided indicate the presence of PFAS in vegetation samples, it does not offer interpretation as to human or environmental exposure or risk.

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Thank you for inviting us to be part of this effort that helps to further both EPA's and New Jersey's understanding of an important issue in the state. This is just one of many Agency efforts that demonstrates EPA's commitment to cooperative federalism.

If you have any questions or concerns about this report, do not hesitate to contact me at (919) 541-2107 or via email at Watkins.tim@epa.gov. I look forward to our continued work together.

Sincerely,

Timothy H Watkins

Timothy H. Watkins
Director

Enclosure

CC:
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Detection, Evaluation, and Assignment of PFAS in Environmental Media from an Industrialized Area of New Jersey

Laboratory Data Report #6: Targeted Analysis of PFCA in Vegetation

Background. EPA/ORD, EPA Region 2, and New Jersey Department of Environmental Protection (NJ DEP) worked together to develop a study to evaluate sources, as well as the nature and extent of PFAS contamination near manufacturing facilities in New Jersey. NJ DEP assumed responsibility for the collection of samples and their shipment to ORD laboratories. ORD was responsible for sample extraction and analysis. ORD personnel involved with laboratory analysis and their roles and responsibilities are provided below in Table 1.

Table 1. EPA Office of Research and Development Analysis and Report Team.

Responsibility	Personnel
ORD Principal Investigators	Andy Lindstrom, Mark Strynar, John Washington
Laboratory Chemistry	John Washington, Brad Acrey, Charlita Rosal
Quality Assurance Review	Brittany Stuart
Management Coordination and Review	Brian Schumacher, Myriam Medina-Vera, Tim Buckley
Report Preparation	John Washington, Kate Sullivan

This 6th report includes results for 24 vegetation samples collected by NJ DEP between November 8 and 10, 2017, and delivered to the ORD lab in Athens, GA on November 14, 2017. The plant matter varied and consisted of grasses, broad leaves, conifer needles, or ferns. The results provided in this report were analyzed under the direction of Dr. John Washington.

Thirteen perfluorinated carboxylic acids (PFCAs), listed in Table 2, were analyzed with Ultra-Performance Liquid Chromatography Mass Spectrometry (UPLC-MS) using methods described within our Quality Assurance Project Plan (QAPP)[1] and that have been generally described in Rankin *et al.*, 2015[2]. These analytes were selected because previous reports have shown them to be of concern. In brief, each sample was divided into three ~1 g aliquots. Each aliquot was extracted with 90%:10% acetonitrile:water followed by a liquid/liquid cleanup. Samples were analyzed using a Waters Acquity UPLC coupled to a Waters Quattro Premier XE tandem mass spectrometer. The reported concentrations are presented as the mean value of triplicate aliquot analysis (Table 3). PFCA concentrations were determined using mass-labeled internal calibration curves for quantitation using a traditional targeted analysis approach. These analyses were performed on samples, field and laboratory blanks, and check standards. Dilution of samples was not performed.

[1] National Exposure Research Laboratory, Quality Assurance Project Plan: Detection, Evaluation and Assignment of Multiple Poly and Per-fluoroalkyl Substances (PFAS) in environmental media from an industrialized area of New Jersey. Prepared for New Jersey Department of Environmental Protection (NJ DEP), D-EMMD-IEIB-010-QAPP-01, September 14, 2017

[2] K. Rankin, S.A. Maybury, T.M. Jenkins, J.W. Washington. A North American and global survey of perfluoroalkyl substances in surface soils: Distribution patterns and mode of occurrence. Chemosphere 161, 333-341 (2015).

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Table 2. PFCA Analyzed in NJ Soil Samples by UPLC-MS.

Acronym	Chemical Name	Formula	CAS Registry Number	Monoisotopic Mass (g/mol)
PFBA	Perfluorobutanoic Acid	$C_4HF_7O_2$	375-22-4	213.9865
PFPeA	Perfluoropentanoic Acid	$C_5HF_9O_2$	2706-90-3	263.9833
PFHxA	Perfluorohexanoic Acid	$C_6HF_{11}O_2$	307-24-4	313.9801
PFHpA	Perfluoroheptanoic Acid	$C_7HF_{13}O_2$	375-85-9	363.9769
PFOA	Perfluorooctanoic Acid	$C_8HF_{15}O_2$	335-67-1	413.9737
PFNA	Perfluorononanoic Acid	$C_9HF_{17}O_2$	375-95-1	463.9705
PFDA	Perfluorodecanoic Acid	$C_{10}HF_{19}O_2$	335-76-2	513.9673
PFUnDA	Perfluoroundecanoic Acid	$C_{11}HF_{21}O_2$	2058-94-8	563.9641
PRDoDA	Perfluorododecanoic Acid	$C_{12}HF_{23}O_2$	307-55-1	613.9609
PFTrDA	Perfluorotridecanoic Acid	$C_{13}HF_{25}O_2$	72629-94-8	663.9577
PFTeDA	Perfluorotetradecanoic Acid	$C_{14}HF_{27}O_2$	376-06-7	713.9545
PFHxDA	Perfluorohexadecanoic Acid	$C_{16}HF_{31}O_2$	67905-19-5	813.9482
PFODA	Perfluorooctadecanoic Acid	$C_{18}HF_{35}O_2$	16517-11-6	913.9418

Quality Assurance

The limits of detection (LOD) and reporting (RL) are defined using a two-mean, one-tailed Student's t-test[3] to verify a significant difference between chemical abundance averaged for the 3 aliquots and that observed in the laboratory process blanks. This approach establishes unique limits for each sample arising from the sample-specific standard deviation among the three aliquot replicates. Samples with no observed peak area in any aliquot are reported as Non-Detect ("ND"). A sample is non-detect if none of the aliquots had a peak area. A sample is less than LOD if a peak area was observed in one more aliquots but the t-statistic for aliquot replicates was less than $t_{critical=.0.05}$ and is reported as "<LOD" in Table 3. A sample is below the RL if the t-statistic is greater than $t_{critical=0.05}$ but less than $t_{critical=.0.01}$ and is flagged as "U" in Table 3. Sample values are reported as process blank corrected (i.e., reported sample concentrations are analytical concentrations minus mean process blank values).

Data were checked for compliance with a number of laboratory and field related quality control evaluation criteria as specified in the project QAPP[1,3]. Recovery was calculated for samples using the recovery internal standard $^{13}C_8$-perfluorooctanoic acid (M8C8) which was added to the field samples in known mass before extraction was initiated. Recoveries averaged 78% and were within recovery acceptance criteria for all samples. Ninety-three percent of check standards concentrations fell within the project's accuracy goal of ±50% of the known concentration. Laboratory precision measurements of the plant samples were variable with the coefficient of

[3] National Exposure Research Laboratory, Quality Assurance Project Plan: Detection, Evaluation and Assignment of Multiple Poly and Per-fluoroalkyl Substances (PFAS) in environmental media from an industrialized area of New Jersey. Prepared for New Jersey Department of Environmental Protection (NJ DEP), Amendment #1 D-EMMD-0031345-QP-1-1. May 2, 2018.

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variation (CV) of valid comparisons of aliquot triplicates meeting the project acceptance goal of <50% in 78% of valid sample/analyte comparisons(>RL) (flagged as "JP1" in Table 3). Remeasurement of the same aliquot was repeated for 7 samples. The CV of repeated measures was within ±50% in 79% of the valid analyte/sample comparisons. Samples not meeting this acceptance criterion are flagged as "JP2" in Table 3.

Results

Concentration results for 24 vegetation samples identified by sample IDs assigned by NJ DEP are presented in Table 3. Targeted results for PFAS in soils collected at the same locations were reported in NJ DEP Report #1[4]. The average of 2 soil field blanks previously reported is also provided in Table 3. There were no duplicate vegetation samples collected. Vegetation sample concentrations are reported as the mean of three sample aliquots in units of mass of PFCA per unit mass of dry solid (i.e., pg/g). Results are reported for 9 PFCAs with carbon chain lengths that range from C4 through C12. Although peak areas were observed for the analytes with longer carbon chain lengths (C13-C18), results could not be confidently quantitated and are not reported.

Concentrations across all analytes and samples ranged from <LOD ("ND" in Table 3) to values that exceeded our calibration curve (flagged "JC1 in Table 3). PFBA was observed in relatively high concentrations in a number of the samples and averaged 70% of the total PFAS observed in samples. Other PFCAs were observed at lower concentrations and were less widely distributed.

[4] NJ DEP Laboratory Data Report #1: Targeted analysis of PFCA in Soil. U.S. EPA/ORD, January 31, 2019.

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Table 3. PFCA Concentrations (pg/g) in Vegetation Samples Determined with Targeted Analysis.

Carbon Length	*C4*	*C5*	*C6*	*C7*	*C8*	*C9*	*C10*	*C11*	*C12*	*C4-C12*
Sample ID	**PFBA**	**PFPeA**	**PFHxA**	**PFHpA**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoA**	**Sum PFAS**
PFVG001	942	157	ND	33.4 U	<LOD	188	ND	30.2	ND	1,350
PFVG002	666	142 U	<LOD	<LOD	ND	48.6 JP1	23.4	512	25	1,420
PFVG003	2,090 JP1	122 U	<LOD	ND	ND	215	<LOD	992	272	3,690
PFVG004	<LOD	<LOD	415 JP1	62.0 JP1	ND	77.8 JP1	24.6 JP1	59.5 JP1	10.6 U	649
PFVG005	1,860	<LOD	<LOD	102 JP1	ND	156 JP1	90.2	97.3	26.2	2,340
PFVG006	802	2,310	180 U	190	<LOD	28.4	ND	8.76 JP1	6.79 U	3,520
PFVG007	<LOD	197	<LOD	ND	ND	94.8	25.2	183	11.2 U	511
PFVG008	1,050	404	409	198	1,120	695	403 U	723	60.1 JP1	5,070
PFVG009	13,700 JC1	490	384	<LOD	<LOD	267	121	686	66.3	15,700
PFVG010	9,430	158 JP1	367	ND	<LOD	107 JP1	ND	ND	<LOD	10,100
PFVG011	8,280	ND	396	45.5	<LOD	ND	ND	40.7	19.9 U	8,780
PFVG012	9,560	192	294	ND	ND	39.1 JP1	162 U	ND	<LOD	10,200
PFVG013	7,750	160	252	<LOD	<LOD	68.7	50.1	29.8	16.7 U	8,330
PFVG014	9,290	<LOD	570	99.7	134 U	198	37.3 U	41.1	18.1	10,400
PFVG015	6,980	203	261	<LOD	<LOD	128	745 JP1	199 JP1	17.1	8,530
PFVG016	7,520	168	274	52.0	<LOD	159	ND	79.7 U	136	8,390
PFVG017	7,550	ND	620	165	277	258	152 U	138 U	272	9,430
PFVG018	8,240	749 JP1	395	ND	<LOD	85.1 U	ND	ND	72.5	9,540
PFVG019	8,720	796	735	351	220	396	ND	91.2 U	125	11,400
PFVG020	7,280	124	337	64.7	ND	138	ND	123	30.1	8,100
PFVG021	6,470	248 JP1	268	<LOD	91.6 U	20.2 U	93.3 U	116 JP1	74.8 JP1	7,390
PFVG022	6,510 JP1	149 JP1	201	ND	ND	<LOD	ND	<LOD	ND	6,860
PFVG023	10,900 JC1	<LOD	1570 JP1	449 JP1,JP2	726 JP1	218 JP2	ND	<LOD	122 JP1,JP2	14,000
PFVG024	8,310	ND	981 JP2	153 JP2	422	404 JP1, JP2	198 U	<LOD	45.5 JP1	10,500
Average FB*	<LOD	<LOD	<LOD	<LOD	<LOD	10.1	<LOD	<LOD	6.1	

ND	No peak area observed
<LOD	Peak area observed in one or more aliquots, but aliquot average not significantly greater than process blanks at T critical = 0.05
U	Sample value less than Reporting Limit: T statistic of aliquots > T critical at α=0.05 but < T critical at α=0.01
JP1	Sample aliquot triplicates do not meet acceptance criteria for precision.
JP2	Aliquot repeated measures do not meet acceptance criteria for precision
JC1	Sample result exceeds the upper calibration range.

*Note: the average of 2 soil field blanks with Sample ID: PFSSFB were collected during the same sampling campaign as vegetation samples.